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LLNL-CONF-663739

Molecular Structure and Ion Transport near Electrode-Electrolyte Interfaces in Lithium-Ion Batteries

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November 4, 2014

249th ACS National Meeting & Exposition
Denver, CO, United States
March 22, 2015 through March 26, 2015

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MOLECULAR STRUCTURE AND ION TRANSPORT NEAR ELECTRODE-ELECTROLYTE INTERFACES IN LITHIUM-ION BATTERIES

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Introduction

The performance of lithium-ion secondary batteries is strongly dependent on the ease of ion transport through electrode-electrolyte interfaces [1]. Ion solvation structures near the interface as well as the chemistry of the electrode surface, in particular the edge termination of graphite electrodes, can impact Li ion transport into and out of the electrode. Understanding these effects is critical to optimizing battery performance. We have performed molecular dynamics simulations of organic liquid electrolytes in contact with graphite electrodes, with and without electric field, to understand the relationship between ion solvation structure and transport near the interface. A prototypical electrolyte consisting of ethylene carbonate (EC) organic solvent containing dissolved $LiPF_6$ salt was studied, in contact with armchair-edge oriented graphite anode electrodes. Various surface terminations of the graphite, including H and OH, were compared.

Methods

Molecular dynamics (MD) simulations were performed with the LAMMPS code [2,3] using the ReaxFF force field [4]. Constant temperature simulations were performed in the NVT canonical ensemble using a three-chain Nosé-Hoover [5,6] thermostat at 330 K, with time steps of 0.25 fs and Nosé frequency of 1333 cm^{-1}. Typical simulations were run for 500–1000 ps, following equilibration for at least 25 ps.

The system under study is shown in Fig. 1 and consists of 120 EC molecules with 8 randomly placed Li^+ and PF_6^- ions (1 M solution) sandwiched between armchair-edge oriented graphite slabs. Various edge terminations of the graphite were considered, including H, OH, and a mixture of H/OH as shown in Fig. 1. The graphite thickness was chosen large enough so that bulk graphite behavior was recovered at the center. Periodic boundary conditions were applied in all directions. Total system size is over 2000 atoms. During MD, the center of the graphite slab away from the interface was held fixed to avoid sliding of the graphite layers. Simulations with conducted beginning with either fully lithiated or fully delithiated graphite, to study Li insertion or extraction from the electrode. For simulations with electric field, the field was applied only across the electrolyte thickness and the uppermost layers of the graphite interface.

Results and Discussion

Ordering of Li near interface. With no electric field applied, the Li^+ ions diffuse within well-defined solvation structures consisting of four carbonyl oxygen atoms from four EC molecules in the first solvation shell [7,8,9]. The PF_6^- ions do not have a well-defined solvation shell [7]. The average association distance between Li and P is ~7.5 Å, which is somewhat longer than the 4.5–5.0 Å found with benchmark density functional theory MD simulations [7].

The Li^+ ions equilibrate into approximately evenly spaced layers parallel to the interface, with the spacing dictated largely by the salt concentration. For simulations with one side of the graphite slab terminated with H and the other with OH, and no electric field applied, the Li^+ show a slight tendency to prefer the OH-terminated surface, as shown in Fig. 2.

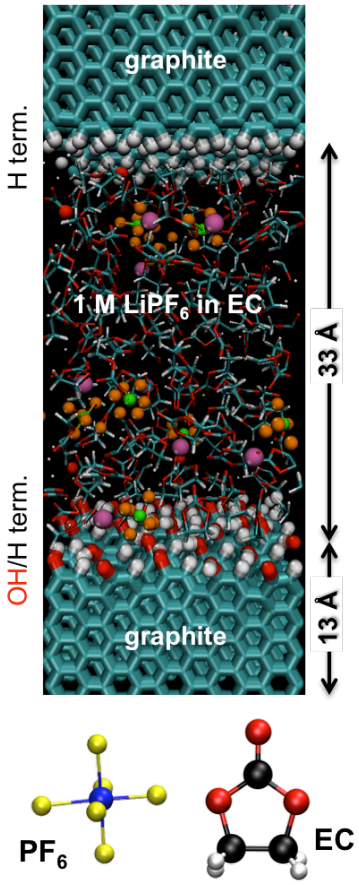

Figure 1. The figure number should be boldface, but the figure caption should be regular typeface, below the figure, with full justification.

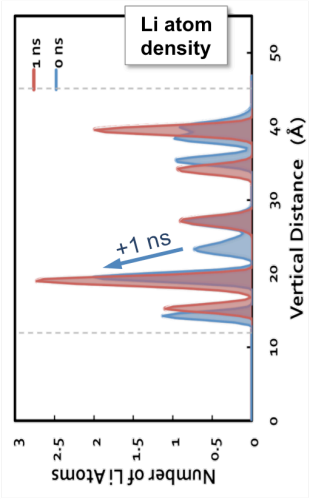

Figure 2. The Li^+ atom density is plotted as a function of vertical distance in the simulation cell shown in Fig. 1, where the gray dotted lines indicated the positions of the graphite slab edges. The lower edge is terminated 50/50 with H and OH, while the upper edge is terminated fully with H. After 1 ns simulation time with no electric field applied, an increase in Li^+ density toward the OH-terminated surface is evident. The nearly regular spacing of Li^+ layers is also apparent.

When an electric field is applied (~0.01–0.2 V/Å) driving Li^+ toward an OH-terminated interface (*e.g.*, pointing in the downward direction for a simulation system like in Fig. 1), the Li ions tend to layer 7–12 Å away from the interface, as shown in Fig. 3, and do not insert into the graphite even after 500 ps, indicated a barrier to insertion related to the OH termination. The same effect is not observed with an electric field driving Li^+ toward a H-terminated interface.

Ion dynamics and Li extraction. Conversely to the Li^+ insertion dynamics, where a termination-dependent barrier was observed as described above, Li extraction from a fully lithiated graphite electrode was observed to occur spontaneously regardless of termination. In fact, Li^+ extraction occurred even against an applied electric field, within 100–200 ps. For the case with an electric field driving Li^+ toward a nearly-fully-lithiated OH-terminated graphite interface, spontaneous extraction of Li^+ against the electric field was occasionally observed; the extracted Li^+ subsequently migrated to the "Li layer" ~10 Å away from the interface (Fig. 3), held by the barrier to re-insertion.

In contrast to the Li^+ dynamics in the presence of an electric field, the PF_6^- counter ions were observed to have much higher mobility, moving freely through the organic solvent when a field was applied. Despite the larger mass and bulkier shape of the PF_6^-, its mobility is higher due to the weak solvation by a poorly-structured solvation shell [7].

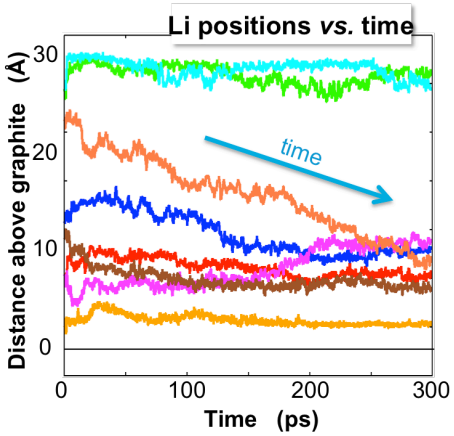

Figure 3. With a strong electric field (0.167 V/Å) driving Li ions toward the OH-terminated graphite interface (at position 0), a barrier to insertion is observed, with Li ions accumulating in a layer ~10 Å away from the interface.

Conclusions

We have used molecular dynamics to study the structure and transport of solvated Li ions in ethylene carbonate (EC) electrolyte in contact with armchair-edge terminated graphite. We find that Li^+ maintains a well-structured first solvation shell in EC even when an electric field is present. The bulkier PF_6^- does not present a strong solvation structure and exhibits higher mobility in an electric field.

We found an energy barrier for Li^+ insertion into graphite, particularly when the surface was hydroxyl terminated. Lithium extraction, however, was facile even against an applied electric field.

Acknowledgement. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Support for this work was provided through Scientific Discovery through Advanced Computing (SciDAC) program funded by U.S. Department of Energy, Office of Science, Advanced Scientific Computing Research and Basic Energy Sciences.

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